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## SOME OBSERVATIONS ON FACTORS AFFECTING THE STRUCTURE OF CALCIUM SOAP LUBRICATING GREASE<sup>1</sup>

BY L. W. SPROULE<sup>2</sup> AND W. C. PATTENDEN<sup>2</sup>

### Abstract

Examination with the electron microscope indicates that the soap particles contained in calcium soap lubricating greases have an unusual structure. They are about  $1 \mu$  long, and consist of fibers coiled in spiral forms, or of two twisted together in a ropelike manner. The effect of two factors on the form of the dispersed soap particles was investigated. The addition of water to stabilize a dispersion of calcium soap in mineral oil was found to orientate the soap particles from minute, nondescript form to fibers having a wavy, loosely coiled appearance. The shearing action associated with the mixing of the grease during its preparation caused the fibers to assume a spiral or twisted form.

### Introduction

Calcium base lubricating greases may be defined as three-component systems consisting of a dispersion of calcium soaps of the higher fatty acids in mineral oil stabilized by a small quantity of water. In view of the colloidal nature of such systems, considerable work has been carried out to determine the size and shape of the dispersed soap particles.

Attempts by Farrington and Davis (3) to photograph the soap particles using an ordinary microscope were unsuccessful. Gallay and Puddington (5, 6) tried to determine the nature of the soap particles by indirect methods, such as viscosity characteristics of soap-oil dispersions, observing the appearance of stream double refraction, etc., but were unable to clearly establish the nature of the particles. Recently Burton (1) has successfully used the electron microscope to indicate the form of the calcium soap particles. His pictures showed that the particles were approximately  $1 \mu$  long, and appeared to consist of tightly coiled fibers. Some time later Farrington and Birdsall (4) published electron microscope pictures of calcium soap lubricating greases which confirmed Burton's work. Ellis (2) has further clarified the structure of the calcium soap particles by comparing electron microscope pictures with X-ray photographs of brass-impregnated plasticene models. He concluded that the soap fibers have the form of a two-stranded rope.

While previous investigations have shown the size and structure of the soap particles contained in calcium soap greases, no information is available

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Contribution from the Technical and Research Department, Imperial Oil Ltd., Sarnia,  
Ont.

<sup>2</sup> Research Chemist.

to indicate the factors responsible for their unusual appearance. This paper describes experiments carried out to determine the effect of shearing forces present during the manufacture of calcium soap greases, and the effect of the presence of the water required to stabilize calcium soap - mineral oil systems on the shape of the soap particles of calcium soap lubricating greases.

### Experimental Work

The effect of the presence of water and of the shearing forces present during manufacture on a calcium soap dispersion in mineral oil may be readily determined by electron microscope examination of samples removed at different stages of the preparation of a typical calcium soap grease.

In preparing the grease, calcium hydroxide is reacted with animal fat in the presence of a small amount of mineral oil at 149° C. (300° F.) and 50 lb. pressure. The "soap concentrate" formed is transferred to an open mixer, provided with a jacket through which steam or cold water is circulated. Agitation of the kettle contents is carried out by double-action paddles, and is continuous throughout the preparation. Mineral oil is added to the soap concentrate until a temperature of about 113° C. (235° F.) is reached. At this point the water necessary to stabilize the soap dispersion is added, generally in two portions. Sufficient mineral oil is now added to obtain a grease of the required consistency.

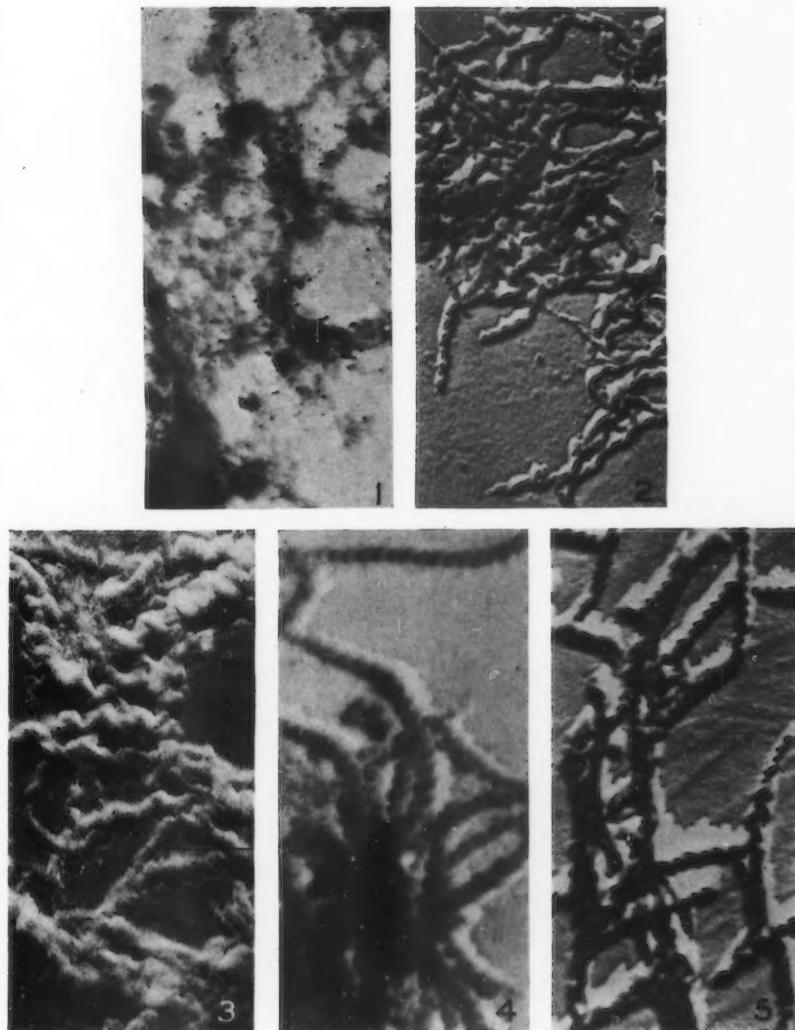
For the purpose of this investigation, five samples of grease were removed at different intervals during its preparation. Details of the samples are given in Table I. The samples were examined at room temperature with the electron microscope.

The samples studied in the preceding experiment were subjected to shearing forces during their preparation. To separate the effect of the two variables, water and shearing forces, a grease was made under conditions where shearing forces were entirely absent.

For this purpose a portion of the grease from the previous experiment was dehydrated by heating at 149° C. (300° F.) for 15 min. under a pressure of 1 mm. of mercury. Approximately 2 gm. of the dehydrated grease was transferred to one arm of a Y-tube. A few drops of water were placed in the second arm and the third arm sealed off. The section containing the dehydrated grease was heated in an oil bath, while that containing the water was maintained at -12° C. (10° F.) by means of a dry-ice bath. At 149° C. (300° F.) it was noted that the soap had settled from the mineral oil, and at 177° C. (350° F.) it was completely dissolved, except for a slight haziness. The grease was made by pouring the melted water into the soap-oil solution at 177° C. (350° F.). On cooling, a grease of good consistency was formed. The grease was examined with the electron microscope at room temperature.

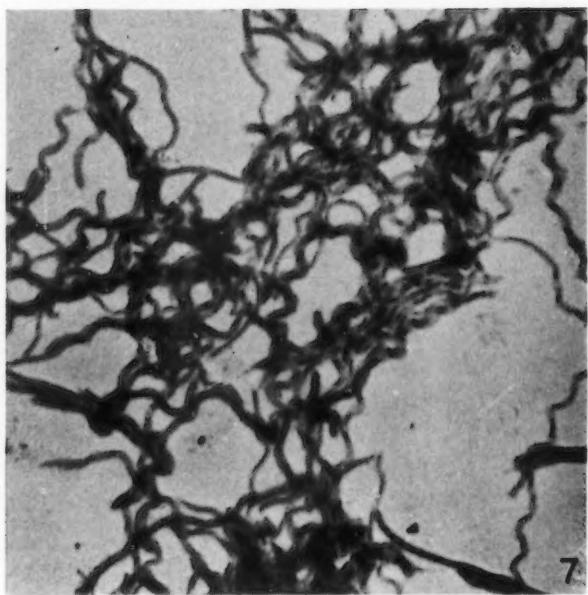
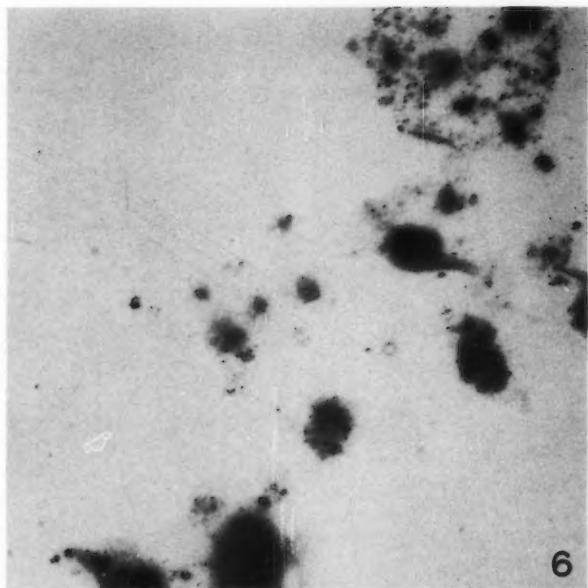
The electron microscope photographs were made by the Department of Physics, University of Toronto. The smear mount technique, as described by Ellis (2) was used, except in those cases where further resolution of the

PLATE I



FIGS. 1-5. Electron micrographs of samples of a calcium soap grease taken at various stages during manufacture.  $\times 24,600$ . FIG. 1, smear mount. FIGS. 2-5, shadow cast.

PLATE II



FIGS. 6 and 7. *Electron micrographs of a calcium soap grease prepared without mixing.*  
 $\times 28,600$ . Both are smear mounts.

TABLE I

SAMPLES REMOVED FOR ELECTRON MICROSCOPE STUDY DURING MANUFACTURE  
OF A CALCIUM SOAP LUBRICATING GREASE

Time from dropping of soap stock into open mixer, min.	Sample No.	History of sample	Appearance of sample when removed from mixer	Composition of grease					
				Parts of weight			% by weight		
				Calcium soap*	Water (added)	Mineral oil**	Calcium soap*	Water (by analy- sis)	Mineral oil**
0	—	Soap stock dropped into kettle	Thick, tacky, semi- fluid	13	0	2.9	81.8	0	18.2
60	—	29 parts oil added	"						
70	1	Sample removed at 113° C. (235° F.)	"	13	0	31.9	29	0	71
75	—	1.0 part water added	"						
85	2	Sample removed at 110° C. (230° F.)	"	13	1	31.9	28.3	2.0	69.7
95-130	—	12.6 parts oil added followed by 1 part water							
140	3	Sample removed at 104° C. (220° F.)	Greaselike	13	2	44.5	21.8	3.4	74.8
145	—	9.6 parts oil added	"						
185	4	Sample removed at 99° C. (210° F.)	"	13	2	54.1	18.8	2.8	78.4
190-360	—	30.9 parts oil added							
370	5	Sample of finished grease removed at 88° C. (190° F.)	"	13	2	85	13	1.6	85.4

\* Inspections of animal fat used in preparation of soap—Saponification value: 196; Iodine No.: 52.8.

\*\* Viscosity of mineral oil at 37.8° C. (100° F.): 65 cks.; Viscosity index: 75.

particles was desired. In these specimens, the shadow cast technique of Wyckoff and Williams (7, 8) using chromium was applied.

The effect of rate of cooling on the structure of the particles in calcium soap greases was not studied in detail. However, experience in plant manufacture has shown that those properties depending upon the nature of the soap particles, such as texture and consistency, are not altered by small changes in rate of cooling. In view of these observations, it is considered that differences in the rates of cooling of greases prepared in the two experiments described will have little effect. However, confirmation of this point awaits the completion of further laboratory investigation.

## Results

The electron micrographs of the samples taken at various stages during the manufacture of a calcium soap grease are shown in Plate I. The picture of the anhydrous soap-oil dispersion (Fig. 1) indicated the soap to be present in the form of a large number of very fine particles or agglomerates of fine particles which have no regular size or shape. Fig. 2, taken after the first addition of water, showed the soap particles to be in the form of fibers. After the second addition of water (Fig. 3), the fibers appeared as loose coils. The addition of further quantities of oil caused the fibers to become more tightly coiled as the preparation of the grease proceeded (Figs. 4 and 5). The change in structure of the soap particles at this stage is not attributed to the addition of oil, but to the effect of the prolonged shearing action required to render the system homogeneous.

Plate II shows electron micrographs of the grease prepared without the use of a shearing action. Fig. 6 illustrates the shape of the soap particles contained in a dehydrated calcium soap grease. The soap was found to be present as very small particles, which confirmed the results of the first experiment. After the addition of water, the soap particles were orientated in the form of fibers, having a wavy or loosely coiled appearance. At present no explanation can be advanced for the wavy appearance of the soap particles, which appears to be characteristic of calcium soap - water - mineral oil systems. Attempts to correlate the appearance of the fibers with models corresponding to various molecular structures were unsuccessful.

From the data obtained in these experiments, it has been possible to account in part for the unusual structure of the soap particles in calcium soap greases. When calcium soap is stirred in mineral oil at elevated temperatures, it becomes dispersed in the form of minute, nondescript particles. The addition of water to this system orientates the particles in the form of fibers having a wavy or loosely coiled form. The shearing action associated with mixing causes the fibers to become tightly coiled.

## Acknowledgment

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## References

1. BURTON, E. F. and KOHL, W. H. *The electron microscope*. 2nd ed. Reinhold Publishing Corporation, New York. 1946.
2. ELLIS, S. G. *Can. J. Research*, A, 25 : 119-123. 1947.
3. FARRINGTON, B. B. and DAVIS, W. W. *Ind. Eng. Chem.* 28 : 414-416. 1936.
4. FARRINGTON, B. B. and BIRDSALL, D. H. *Oil Gas J.* 45-46 : 268. 1947.
5. GALLAY, W. and PUDDINGTON, I. E. *Can. J. Research*, B, 22 : 161-172. 1944.
6. GALLAY, W. and PUDDINGTON, I. E. *Can. J. Research*, B, 22 : 173-181. 1944.
7. WILLIAMS, R. C. and WYCKOFF, R. W. G. *J. Applied Phys.* 15 : 712-716. 1944.
8. WILLIAMS, R. C. and WYCKOFF, R. W. G. *J. Applied Phys.* 17 : 23-33. 1946.

## PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

### XXVIII. PILOT PLANT RECOVERY OF *levo*-2,3-BUTANEDIOL FROM WHOLE WHEAT MASHES FERMENTED BY *AEROBACILLUS POLYMYXA*<sup>1</sup>

By J. A. WHEAT<sup>2</sup>, J. D. LESLIE<sup>2</sup>, R. V. TOMKINS<sup>2</sup>,  
H. E. MITTON<sup>2</sup>, D. S. SCOTT<sup>2</sup>, AND G. A. LEDINGHAM<sup>3</sup>

#### Abstract

Whole wheat mash fermented by *Aerobacillus polymyxa* was stripped of ethanol, screened, and concentrated. The resulting syrup was passed through a steam stripping column, and the *levo*-2,3-butanediol in the condensate was recovered by rectification. The composition of intermediate materials and products, performance of pilot plant equipment, and data and recommendations for the design of a large scale plant are given. Corrosive conditions are indicated and possible materials of construction suggested. A quantitative flow sheet and cost estimates for a commercial plant with a capacity of 1000 bu. of wheat a day are included. The daily output of such a plant is estimated to be 8460 lb. of diol (95.5% recovery), 675 gal. of 95% ethanol, 3900 lb. of dried bran, and 25,300 lb. of dried solubles. The initial cost of such a plant is estimated at \$500,000. From estimates of raw materials and energy requirements the total cost of production of diol is calculated to be 17.3 cents per lb. when wheat costing \$1.10 per bu. is fermented.

#### Introduction

The recoverable products of a grain mash fermented by *Aerobacillus polymyxa* are ethanol, *levo*-2,3-butanediol, and residual solids. *Aerobacter aerogenes* produces a smaller amount of ethanol and a correspondingly greater amount of diol which is predominantly the *meso*-isomer (22). The physical properties of the two diol isomers other than the freezing points of aqueous solutions are very similar; consequently, any method of recovery applicable to one could be applied to the other with only minor changes in the process.

Since ethanol is the lowest boiling constituent it is easily recovered by distillation. Diol, however, has a boiling point above that of water (179° C. or 354° F. at 760 mm.) and cannot be recovered by a simple distillation of the fermented mash. The initial steps of all suggested recovery methods are similar, and consist of removal of ethanol, filtration or screening, and concentration of diol and solids by evaporation. Ethanol can be recovered either by a separate operation or during evaporation. The former method was used in the pilot plant and the latter method is recommended by Callaham (5) for the recovery of ethanol from mashes fermented by *A. aerogenes* and has also been used to recover industrial ethanol from molasses fermented by yeast (17).

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<sup>2</sup> Chemical Engineer, Industrial Utilization Investigations.

<sup>3</sup> Mycologist, Industrial Utilization Investigations.

The methods that have been suggested for the recovery of diol from evaporator syrup are spray drying (12), drum drying (12), chemical conversion (18), dialysis (7), solvent extraction (12, 13, 16), ethanol precipitation (21), kerosene distillation (12), and steam stripping (4, 5). The methods that have been tested in these laboratories will be briefly described.

*Drum Drying.*—This method was tested by J. D. Leslie and D. Rose in the experimental laboratory of the J. P. Devine Manufacturing Co. at Mount Vernon, Illinois, in 1943. It was found that with a vacuum of 28 in. of mercury and a steam pressure of 60 p.s.i. gauge, the lowest diol concentration that could be obtained in the dried solids was 7.6%. At higher steam pressures or lower drum speeds the solids began to decompose. Because of these results no further work was done on this method.

*Dialysis.*—Laboratory tests showed that large equipment would be required for large scale production. No work on a pilot plant scale was performed.

*Ethanol Precipitation.*—In this pilot plant, and elsewhere (21), syrup was first thoroughly mixed with ethanol, either with or without previous chemical treatment, the solids were allowed to settle, and the supernatant liquid was drawn off. Ethanol and diol were then recovered from the decantate by distillation. The remaining solids may be treated with ethanol a second time and then dried.

*Steam Stripping.*—In this method syrup and steam were passed countercurrently through a packed column, operated under pressure to favor vaporization of diol. A description of this method as applied to the recovery of the *meso*-isomer is given by Blom *et al.* (4), and a more complete flow sheet is given by Callaham (5). The present paper gives the results obtained in the pilot plant for recovery of *levo*-butanediol by steam stripping. In commercial production the diol would be condensed from the vapors leaving the top of the stripping column, by continuous countercurrent water scrubbing in a packed or plate column.

After the diol has been separated from the solids it must be freed of water and impurities. In commercial production the by-product ethanol would be concentrated and purified and the suspended and soluble solids would be dried. If the solids were to be dried separately, a rotary drier could be used for the suspended solids and a drum drier for the stripping column residue. As an alternative, the solids could be mixed and the mixture dried in a rotary drier.

The recovery units were designed for a capacity of about 900 gal. of mash per week, and the operations investigated included ethanol stripping, decantation, filtration, screening, evaporation, ethanol precipitation, steam stripping, purification, and drying. In addition to the results obtained in the pilot plant, a suggested quantitative flow sheet for the commercial production of butanediol together with estimates of fixed, material, and processing costs are included in this paper.

### Pilot Plant Equipment, Operations, and Experimental Results

Fig. 1 is a diagrammatic flow sheet of the pilot plant showing the important vessels and flow paths. The vacuum distillation unit for purifying diol is not shown. The usual recovery procedure was to process the mash of two fermentations, about 900 gal., and to carry it through to the final recovery stages before starting another batch. Thus, although some of the units were designed for continuous operation, they were operated continuously only long enough to process one batch. Other operations, such as decantation and ethanol precipitation, were true batch operations.

#### *Mash Composition*

A description of the mashing and fermentation methods and results will be submitted in a subsequent paper (2). An initial mash concentration of approximately 15%, or 34 gal. per bu., was used for nearly all fermentations. A constant concentration was not obtained because of varying amounts of added water and sparged steam. Product concentrations in the fermented mash varied both for this reason and because of the fermentation conditions. To correct for variations in mash concentration, all yields and concentrations were calculated either to the basis of initial weight of wheat or to that of a 15% mash concentration. Assuming the initial wheat to be 50% starch, a fermentation efficiency of 90%, and a diol-to-ethanol ratio of 1.50, the fermented mash would be 2.32% by weight diol and 1.54% ethanol (2). A 60 lb. bushel of wheat would yield 8.91 lb. of diol and 5.91 lb. of ethanol. The fermented mash has a total solids concentration of 6.47%. Calcium carbonate added to the mash accounted for about 10% of the total solids, and the remainder was unfermented material from the wheat and malt. About one-half of the solids was soluble and an amber colored liquid was obtained on filtration. The specific gravity of the fermented mash was 1.020 and that of the filtrate was 1.010. Fermented mash also contained small amounts of diacetyl, acetoin, organic acids, and unfermented carbohydrate. The method used to analyze fermented mash and other pilot plant products has been described (11).

#### *Ethanol Recovery*

The first step of the recovery process was to strip ethanol from the fermented mash in a copper, bubble cap, beer column. The column was 2 ft. in diam. with 22 plates on 17-in. spacings. Each plate had 14 bubble caps which, except for those of the top two plates, were not slotted. Instead of slots, the edges of the caps were  $1\frac{1}{4}$  in. from the plates. This construction was used because bran particles would have plugged the slots. Ethanol was removed at a concentration of 150 proof, and was passed through a cooler, rotameter, and tail box to a 750 gal. steel storage tank. Heat was supplied at the base of the column by either a steam coil or steam sparge. (During operation only the coil was used, but sparged steam was necessary in starting up.) The feed rate to the column was controlled with an orifice meter and controller. The steam supply was automatically controlled by the pressure drop across the

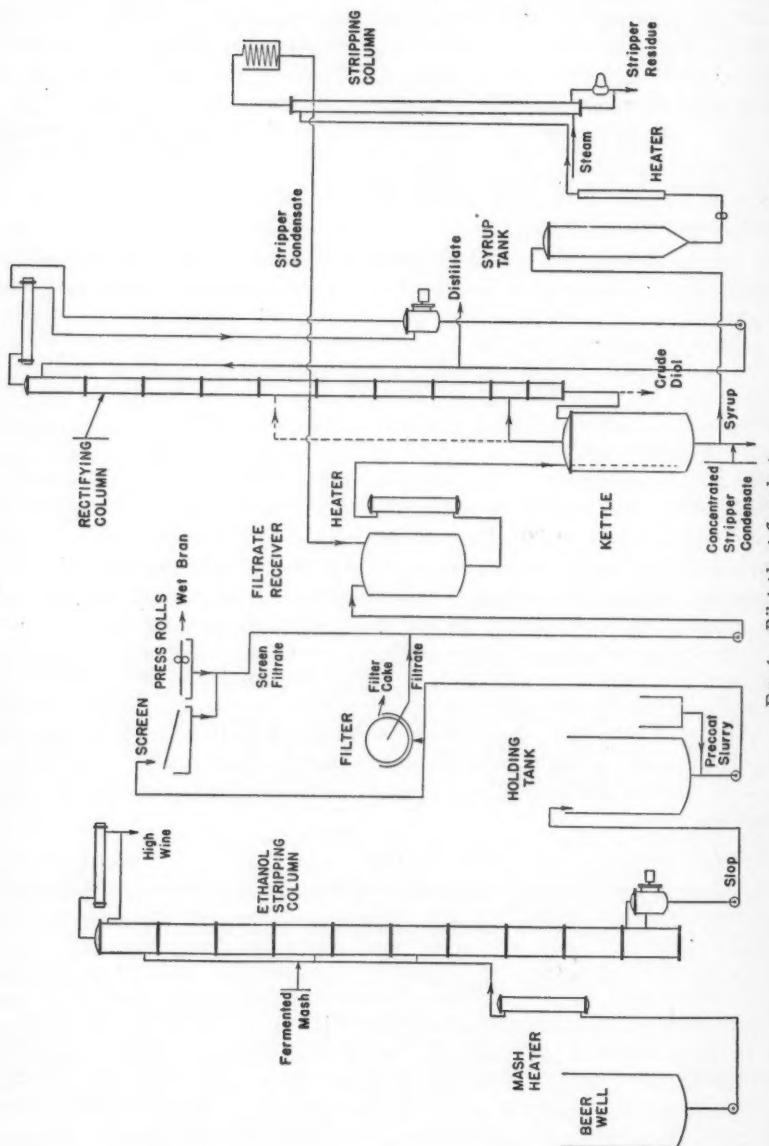


FIG. 1. Pilot Plant flow sheet.

column and the slops discharge was controlled by a liquid level controller in a tank opposite the base of the column. The distillate composition was regulated manually according to the temperature at the top of the column and the hydrometer reading of the material in the tail box. The ethanol content of the slops was estimated by condensing a portion of the vapors below the bottom plate and determining the ethanol concentration with a hydrometer, as is the practice in the production of industrial ethanol and distilled liquors.

The feed rate to the beer column was 200 to 250 gal. per hr. or 65 to 80 gal. per hr. per sq. ft. of cross section. The unit gave satisfactory performance when fed at either the eleventh or fifteenth plate from the bottom. During the operating period, when conditions were steady, the unit was operated at a reflux ratio (reflux rate divided by take-off rate) of 10 and a product concentration of 150 proof. The high wine contained 0.1% diol, which is a diol loss of 0.08%; and the slops contained 0.01% ethanol, which is an ethanol loss of 0.67%. The plate efficiency of the column was 25%. A low value was expected for this column because of the construction of the bubble caps of the bottom 20 plates.

No difficulty was experienced in transferring sufficient heat to the boiling slops, and heat transfer coefficients of the order of 400 to 500 B.t.u. per hr. per sq. ft. per °F. at a temperature difference of 45° F. were obtained. The nominal retention time in the beer column was 12 to 15 min.

The composition and purification of the high wine obtained from the ethanol stripping operation has been discussed by Tollefson, Wheat, and Leslie (19).

#### SUSPENDED SOLIDS REMOVAL

##### *Decantation and Filtration*

After about 16 hr. settling in the holding tank, approximately 60% of the slops could be decanted as a clear liquid. The thickened slops were filtered with an Oliver vacuum filter of the rotary, precoat type, with a drum 3 ft. in diam. and 2 ft. long. After numerous operational difficulties caused by foam had been eliminated, filtration rates of 3 gal. per hr. per sq. ft. were obtained. Filtration was abandoned because of large diol losses (3 to 6%) and the high precoat content of the filter cake. Instead, a simple screening operation was used.

##### *Screening and Pressing*

In these operations whole slops were screened and the resulting solids were pressed to remove a large portion of the liquid phase. The vibrating screen was a Model 35 Dillon, 1.5 ft. wide and 4 ft. long. It was operated at approximately 30 vibrations per second by means of an eccentrically weighted fly wheel. A section of the screen, 2 in. wide, was used for washing experiments. Wash water was distributed from three 1 in. pipe caps placed longitudinally along the screen. Each cap was drilled with five 1/32 in. holes and the amount of wash water was measured with a rotameter. The washings were mixed with the screen filtrate. Wet bran fell through a chute to the press

on the floor below. This press consisted of a pair of washing machine wringers driving an endless belt of 60 mesh screen which carried the bran between the wringers.

Tests were made on the vibrating screen with both 40 mesh and 100 mesh screen. The difference in performance between the two was insignificant, showing that solids not removable by filtration are present in slops in two definite particle sizes: those retained by 40 mesh and those that pass 100 mesh. For calculating material balances and studying screening data, solids that pass 100 mesh were arbitrarily defined as soluble. The ratio of insoluble solids to total solids in slops was determined from the mean value of 18 tests of the ratio of total solids in slops to total solids in screen filtrate. From these results it was found that 13% of the solids in slops was insoluble. The screen could be operated at 5000 gal. per hr. per ft. of width without overloading but in pilot plant tests, other than washing experiments, lower rates were used.

It can be shown by theoretical calculation that the percentage diol and soluble solids retained by the screen are functions of only the total solids in slops, screen filtrate, and screenings; or of the insoluble solids in slops and screenings. At a constant ratio of insoluble to total solids in slops and a constant total solids content of screenings, the percentage diol and soluble solids retained by the screen increases with increasing solids content of slops, regardless of the initial diol concentration. Since the total solids content of slops varied throughout each run as well as from one run to another, a variable screen performance was obtained. Because the screen was seldom operated at full capacity, variations in the composition and rate of feed could not be expected to affect the solids concentration of the screenings. Therefore, the value obtained in the pilot plant should be applicable to large scale operations in which the screen is not overloaded. In 13 tests, this value varied from 12.8 to 15.6% with a mean of 13.5%. The average amounts of diol and total solids retained on the screen were 5.5% and 15.3%, respectively. These values varied from 3 to 7% for the diol retained and from 9.5 to 21% for the solids.

Most of the liquid in the screenings was very loosely bound and could be removed by a mechanical pressing operation similar to that used in distilleries. The results obtained with the washing machine wringers corresponded to those obtained with commercial types of presses. After pressing, the screenings had a solids concentration of about 31%. This means that 75% of the liquid phase, and therefore 75% of the diol, was recovered by pressing.

In commercial production it would be desirable to decrease the diol content of the bran in order to increase recovery and also to improve the quality of the bran as a livestock feed. The simplest method of accomplishing this is to wash the bran as it moves across the screen. To evaluate the experimental results, they were compared with the theoretical results of one equilibrium contact. In the calculations it was assumed that washing would not change the total weight of screenings, i.e., that the insoluble solids concentration of

the screenings would not change. Amounts of water varied from 9 to 19% of the slops and recoveries varied from 50 to 100% of one equilibrium contact. A more efficient system of water distribution would improve washing performance and for large-scale production a screen at least 6 ft. long, with wash water well distributed over the middle third, is recommended.

#### EVAPORATION AND RECTIFICATION

Filtrate from either the filter or vibrating screen was pumped to the kettle, which consisted of a mild steel cylindrical shell with a steam coil of 80 ft. of 1½ in. copper tubing. It was charged with approximately 100 gal. of filtrate and, as evaporation proceeded, feed was added by manual regulation. From one to two liters of Turkey Red Oil was added to the initial charge.

The vapors from the kettle entered the rectifying column either at the base or near the middle. The reboiler of the column was a calandria type heating element consisting of 31 one-inch tubes 15 in. long. The condensate was pumped to the instrument panel where both reflux and take-off were manually controlled and measured with rotameters. The steam supplied to the kettle was automatically controlled by the pressure drop across the column. The column could be operated at automatically controlled pressures below atmospheric but nearly all evaporations were carried out at atmospheric pressure. Because of the very slight increase in boiling point with increasing diol concentration, temperature cannot be used to regulate reflux and take-off. Instead, the reflux ratio must be set and the column performance determined by material balances.

When the syrup was to be treated with ethanol, the vapors from the kettle were fed to the middle of the column and a portion of the diol removed at the base. Since the amount of diol vaporized was very small, particularly at the beginning of a run, diol was not withdrawn continuously but only whenever the temperature at the bottom of the column indicated a diol concentration of 60 to 80%. If the syrup was to be steam stripped, the vapor from the kettle was fed to the bottom of the column, the calandria was not used, and only water was removed. In either method, after all of the filtrate had been added to the kettle, evaporation was continued until approximately the desired solids concentration had been reached. The syrup was then blown with compressed air to the syrup storage tank.

#### *Evaporation*

The evaporation of decantate plus filtrate, slops, and screen filtrate was studied in the pilot plant. The distillate from all three materials was essentially water but also contained diol and some of the more volatile compounds formed during the fermentation and subsequent treatments. The diol content depended upon the operation of the rectifying column and will be discussed below. The most important of the impurities was an appreciable amount of acid. Most distillates were at a pH of from 3 to 5 and contained up to 0.4% acid expressed as weight per cent acetic acid. This material was found to be very corrosive to iron pipe, especially at points of contact with copper or brass.

Decantate and filtrate were occasionally concentrated to 50 or 60% solids but the syrup so formed was very viscous and difficult to handle. A solids concentration of 40% would be more satisfactory both for the evaporation and for the following operation. A large number of measurements of the over-all coefficient of heat transfer to boiling beer were made. These are not directly applicable to larger evaporators constructed of tubes rather than a coil but some useful information was obtained. The heat transfer coefficient to boiling water, determined immediately after the coil had been cleaned with a boiling 2% sodium hydroxide solution, was 750 B.t.u. per hr. per sq. ft. per °F. at a temperature difference of 15° F. and 920 at a difference of 20° F. The heat transfer coefficient decreased during evaporation and consequently the temperature difference increased to maintain a constant rate of boiling. This decrease in the coefficient was caused by increasing solids concentration and fouling of the coil. No attempt was made to differentiate between the effect of solids concentration and that of fouling in the evaporation of filtrate or slops, but an estimate of the effect of fouling in the evaporation of screen filtrate was made and is discussed below. The heat transfer coefficient to boiling filtrate at the start of an evaporation varied from 100 to 500 and at the end from 60 to 200 B.t.u. per hr. per sq. ft. per °F. The initial value depended on the cleanliness of the coil and to some extent on the composition of the filtrate. After each run the kettle was washed with hot water and occasionally with sodium hydroxide. It was also washed at frequent intervals with ethanol when high wine was rectified.

It was more difficult to evaporate slops than filtrate. Only three tests were made, one at atmospheric pressure, another at 15 in. of mercury vacuum, and a third at 25 in. vacuum. At atmospheric pressure, the initial heat transfer coefficient was 500 B.t.u. per hr. per sq. ft. per °F. but it decreased rapidly after the solids concentration had reached 16% and at 20% the coefficient was 16. At 15 in. vacuum the coefficient was about 200 until a solids concentration of 22% was reached and then it decreased to 13 at 26%. At 25 in. vacuum the coefficient was 70–90 to a solids concentration of 40% and then decreased to 36. The evaporation of slops is not practical because of the low heat transfer coefficients and also because of the difficulties that would be encountered in handling syrup containing large particles of bran.

Screen filtrate was evaporated more easily than slops but with greater difficulty than filtrate. The resulting syrup, however, contained no large particles and was not appreciably more difficult to handle than the syrup from decantate and filtrate. Solids concentrations of from 35 to 40% have been obtained but 30% would be recommended for commercial production for ease of handling and to reduce decomposition and fouling in the evaporator. The initial value of the over-all coefficient of heat transfer varied from 300 to 500 and the final value from 20 to 200 B.t.u. per hr. per sq. ft. per °F. It was observed that the heat transfer to material containing large amounts of unfermented starch was appreciably lower than that to material from complete fermentations. Hot water washes between runs did not clean

the coil thoroughly after the evaporation of screen filtrate and it was necessary to use sodium hydroxide after each run. Even then, a thin, hard film, removable by scraping, formed on the coil over a period of approximately six months.

To determine the extent of fouling and diol decomposition, screen filtrate concentrated to 20% solids was refluxed until the heat transfer coefficient was below 100. A plot of the coefficient against time (Fig. 2) shows that fouling occurred rapidly. The extent of solids deposition and fouling would be

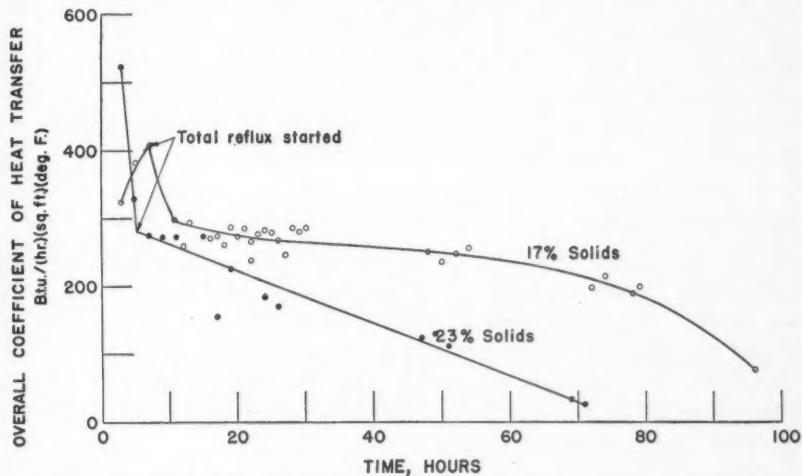


FIG. 2. Decrease in the over-all coefficient of heat transfer on refluxing partially concentrated screen filtrate.

reduced in forced circulation, long tube evaporators, but frequent washing of the tubes with sodium hydroxide, and mechanical cleaning at longer intervals, would probably be necessary. To determine whether or not diol decomposition was appreciable, material balances were made over the whole operation. For reflux times of 25, 52, and 96 hr. the diol losses were 3.2, 9.7, and 4.5%, respectively. These experiments show that some diol decomposition occurs but it would not be appreciable in commercial production where the retention time of an evaporator would be relatively short compared with that used in these tests.

In this work the diol concentration of the distillate ranged from 0.4 to 0.14% and losses were about 5%. Reflux ratios (reflux rate divided by take-off rate) of about 0.5 were used in most evaporation. The plate efficiency of the rectifying column was tested with both diol-water and ethanol-water systems and was found to be approximately 25%. In view of the low efficiency of the rectifying column, the most reliable method for designing columns for commercial production would be to use accurate vapor-liquid equilibria data and the usual methods of estimating allowable vapor velocities and plate efficiencies.

### *Rectification*

In this operation diol losses in the distillate were appreciably greater than for evaporation because there were fewer plates above the feed. At a reflux ratio of 1.0 losses were approximately 15%. At temperature differences of about 70° F., over-all coefficients of heat transfer of about 250 B.t.u. per hr. per sq. ft. per °F. were obtained in the reboiler. About one-half of the diol was removed from the reboiler at a concentration of 40 to 70%. This material was dark green or brown in color and in addition to diol and water it contained organic acids both free and combined, ammonia and other nitrogen compounds, and solids. The presence of solids was due to entrainment from the kettle to the rectifying column. Analysis of a typical crude diol showed 4.5 lb. of ammonia; 4.25 lb. of free acid and 0.6 lb. of ester, calculated as acetic acid; and 1.5 lb. of solids per 100 lb. of diol.

### DIOL RECOVERY

#### *Ethanol Precipitation*

Syrup was mixed with 95% ethanol in the syrup storage tank and the mixture was allowed to settle. In a few tests the addition of ethanol was preceded by the addition of lime. After settling, the decantate was pumped off and recycled with fermented mash, or diol and ethanol were recovered by distillation. The solids were removed from the tank and filtered through three or four layers of cheese cloth. The solids were discarded and the filtrate was added to the decantate.

Although ethanol extracted a large portion of the diol it also extracted an almost equally large portion of the solids. In most tests the precipitated solids settled rapidly to an easily handled granular precipitate, with a sharp layer between solids and decantate. The mean of six tests showed that 83.3% of the diol and 76.7% of the solids were extracted. In one test, in which the syrup was first treated with lime, 94.5% of the diol and 33.7% of the solids were extracted. A lime treatment, therefore, would be used industrially and the first precipitate would probably be retreated with ethanol. Ethanol would be recovered from the decantate by distillation and the resulting crude diol could be treated in several ways. Walmesley and Davis (21) propose a vacuum distillation and report an over-all recovery of diol from fermented molasses of 90%. It is doubtful whether a vacuum distillation could be successfully applied at this stage of the process for the recovery of diol from whole wheat mashes. The diol-to-solids ratio would be about 0.85 while that reported by Walmesley and Davis is 2.5. The composition of the solids extracted by ethanol differed from that of the precipitated solids since in one test the decantate contained 81% of the nitrogen and 72.5% of the solids of the syrup. Therefore it is not advisable to recycle the diol-solids mixture with syrup because of the risk of increasing the ethanol soluble solids to such an extent that the method would no longer be practicable.

### *Steam Stripping*

The steam stripping column consisted of a 20 ft. length of 6 in. pipe. Initially, 1 in. raschig rings were used as packing but they were replaced as soon as 1½ in. spheres were available, although there was no evidence that rings were not satisfactory. After about a year of operation with spheres and with syrup from screen filtrate, the packing was found to be partially plugged and the raschig rings were replaced. A steam flow controller was installed at the inlet to the column and the pressure at the top of the column was controlled at 40 p.s.i. gauge. Considerable difficulty was experienced in securing a constant feed rate because of the high viscosity of syrup and the low flow rates required. In July, 1947, a proportioning pump was installed and syrup was pumped from an open tank in which volume measurements were made. The syrup was screened through 60 mesh wire cloth to prevent large particles of rust from plugging the check valves of the pump.

Syrup was preheated by a 6 ft. steam jacket around the feed pipe. The residue at the base of the column was collected in a vessel under pressure, and at intervals this vessel was isolated from the column and the residue drained. A float type, liquid level controller installed in February, 1947, proved to be more satisfactory. The residue was usually discarded but a number of drum drying tests and analyses of the dried material were performed. The vapor from the top of the column was condensed and concentrated in the kettle before purification by vacuum distillation.

The results obtained with syrup from decantate and filtrate are shown in Table I. At the time, it had not been possible to maintain a constant feed

TABLE I

STRIPPING COLUMN RESULTS ON SYRUP FROM DECANTE AND FILTRATE

(Operating pressure: 40 to 42 lb. per sq. in. Column packed with 1-in. raschig rings)

Feed rate, lb. per hr. per sq. ft.	44	111	204	503	505*
Steam rate, lb. per lb. feed	26.2	16.4	5.7	2.3	3.0
Recovery, %	80.5	97.1	92.5	98.1	99.2

\* Column packed with 1½-in. spheres.

rate to the column over long periods. To secure the information presented, samples of condensate and residue were collected over one-hour periods during which the feed rate appeared to be constant. Material balances were calculated from the analyses of the four fluids entering and leaving the column and from the volume of condensate. The calculated residue rate was then compared with the measured rate, and in all the tests reported in Table I the agreement was within 8%. Neither height of a theoretical plate nor height of a transfer unit was calculated with these data and none of the stripping column residue was retained for drying tests.

The accumulation of material in the column partially plugged the packing, and the pressure drop increased until eventually the column flooded and syrup was carried over the top with the diol-water vapor. This accumulation of material was not caused by excessive liquid or vapor rates but by the nature of the syrup. The only method by which diol could be steam stripped from syrup was to operate the column until flooding occurred and then to wash out the accumulated solids. This procedure was followed to determine how long the column could be operated under various conditions before flooding. The extent of accumulation was followed by observing the pressure drop across the column throughout a run. The pressure drop increased slowly from about 0.5 in. of water per foot of packing to 1.5 in. and then increased rapidly to 5.5–7.0 in., when flooding occurred and solids were entrained by the vapor at the top of the column. When direct measurement of the feed was possible, samples were taken over several one-hour periods during each run for analyses and calculation of material balances. Total material and diol balances generally checked to within experimental error, but there was a consistent loss of about 15 to 30% of the solids fed to the column at a solids concentration of 18.5%, and a 25 to 50% loss at a solids concentration of 23.6%. The solids were removed at the end of a run by running water at 40° to 50° C. at a rate of 1750 gal. per hr. per sq. ft. through the column for half an hour. During shutdown periods the column was left full of water. From the fact that the initial pressure differential did not steadily increase it is concluded that this procedure is sufficient to clean the column and that cycles can be repeated indefinitely.

The flooding times at various syrup solids contents and operating conditions are given in Table II. Flooding times at rounded values of solids content and feed rate were obtained by interpolation and are given in Table III.

From the analyses of the samples taken over one-hour periods the values of  $(H_t)_{OG}$  were calculated and are given in Table II. Equation (1) for equimolar counter diffusion given by Colburn (6) was used to calculate the number of transfer units.

$$(N_t)_{OG} = \int_{y_1}^{y_2} \frac{dy}{y^* - y}. \quad (1)$$

$(N_t)_{OG}$  = Number of transfer units based on change in gas concentration.

$y$  = Mole fraction of diol in the vapor.

$y^*$  = Equilibrium mole fraction of diol in the vapor.

The height of a transfer unit was then calculated from Equation (2)

$$(H_t)_{OG} = \frac{H}{(N_t)_{OG}}. \quad (2)$$

$H$  = Height of packing (17 ft. in the pilot plant column).

The vapor-liquid equilibria data of Tomkins *et al.* (20) at 45 and 75 p.s.i. abs. were interpolated to obtain the equilibria data at 55.7 p.s.i. abs., which was the average of the top and bottom pressures of the column. To estimate

TABLE II

FLOODING TIMES AND TRANSFER UNIT HEIGHTS AT VARIOUS OPERATING CONDITIONS OF THE STRIPPING COLUMN

Syrup solids, %	Syrup rate, lb. per hr. per sq. ft.	Steam rate, lb. per hr. per sq. ft.	Flooding time, hr.	$(H_t)_{OG}$ , ft.
14.5	277	745	4.8	1.7
	293	680	4.3	—
17.0	169	610	12.3	4.0
	214	610	6.2	—
	223	680	9.0	2.0
18.5	161	610	14.8	3.7
	163	680	8.5	3.2
19.6	177	610	7.1	—
	168	610	5.2	—
	174	680	4.5	—
	164	745	2.6	—
	231	680	3.4	—
19.9	212	610	4.5	—
23.6	145	610	7.0	4.6
	148	680	4.3	4.6
	206	610	4.3	2.9

TABLE III

EFFECT OF SOLIDS CONTENT OF SYRUP ON THE FLOODING TIME OF THE STRIPPING COLUMN AT VARIOUS FEED AND STEAM RATES

Rates lb. per hr. per sq. ft.	Syrup 160	Steam 610	Syrup 210	Steam 610
Solids content of syrup, %	Flooding time, hr.			
17.0		12.3		6.2
20.0		9.0		4.5
23.6		6.2		4.3

the diol concentration in the vapor in equilibrium with syrup it is necessary to know the effect of solids on the relative volatility of diol and water. Direct tests were performed in the Othmer still described by Tomkins *et al.* (20) to determine the effect of solids. The still was operated at atmospheric pressure, and, because of the foaming in the still, solids concentrations lower than those of actual syrups had to be used. The results obtained are given in Table IV. A closer approximation to the equilibrium diol concentration in the vapor is obtained by calculating the diol concentration in the liquid on a solids-free

TABLE IV  
EFFECT OF SYRUP SOLIDS ON THE RELATIVE VOLATILITY OF DIOL AND WATER

Solids content, weight %	Liquid composition, wt. % of diol	Equilibrium vapor composition for pure solutions (20), wt. % diol	Observed vapor composition, wt. % diol	Variation, %
4.94	Total basis . . . . . 2.08	0.28	0.33	+15
	Solids free basis 2.19	0.29		
11.50	Total basis . . . . . 4.20	0.58	0.68	+15
	Solids free basis 4.76	0.66		+3

basis rather than a total basis. Blom *et al.* (4), however, report that the solids should be considered as water, that is, that a total basis should be used.

The estimates of  $(N_t)_{OG}$  given in Table II are only approximate because the syrup was fed to the column at 185° F. rather than the boiling point of 287° F. and because of heat loss from the column. Cold feed increased the actual liquid rate in the column by 9.5% and heat loss increased liquid rate by about 40% at a feed rate of 160 lb. per hr. per sq. ft. The vapor rate at the top of the column was less than the steam rate by the amount of steam required to heat the feed and to supply the heat loss. Condensation at the top of the column to heat the feed would give a lower diol concentration in the exit vapor than that actually existing at the top of the packed section and would also make the actual diol concentration in the liquid lower than the diol concentration of the syrup. Thus, if actual concentrations at the top of the packing could have been used, values lower than those given in Table II would have been obtained for  $(H_t)_{OG}$ .

The over-all coefficient of heat transfer from steam to syrup was determined in an experimental heat exchanger consisting of a  $\frac{3}{8}$  and a 1 in. I.P.S. pipe in a 4 in. I.P.S. steam jacket. The rate of heat transfer was determined from the syrup rate and the increase in temperature of the syrup. The specific heat of the syrup was assumed to be 0.8 B.t.u. per lb. per °F. The results obtained are given in Table V.

TABLE V  
HEAT TRANSFER FROM STEAM TO EVAPORATOR SYRUP

(Diol content of syrup, 10.26%; solids content of syrup, 25.1%)

Steam temperature, °F.	275	248	275	275
Mean temp. difference, °F.	153	144	150	150
Syrup rate, lb. per hr. per sq. ft.	70400	85600	76900	17000
Over-all heat transfer coefficient, B.t.u. per hr. per sq. ft. per °F.	167	127	181	22

CONCENTRATION OF STRIPPER CONDENSATE AND PURIFICATION OF  
CRUDE DIOL

The stripper condensate had a diol concentration of from 1.5 to 2.0% by weight, the remainder being mainly water and finely divided solids. It contained 7 to 10 lb. of acid, calculated as acetic acid, per 100 lb. of diol, and about the same amount of ammonia. The ester content was usually negligible because of the high water concentration. The condensate was evaporated in the beer kettle and rectifying column and water taken off overhead. This operation concentrated the diol and solids to form a crude diol. The evaporation was continued until the volume of crude diol was 25 gal. or less, as this volume was easily handled in subsequent operations. Because of the acidity of the condensate nearly all of the ammonia remained in the crude diol. A portion of the acid, however, was removed in the distillate. The crude diol obtained in the pilot plant contained both dissolved and suspended iron compounds resulting from corrosion of the kettle. The composition of several crude diols is given in Table VI.

TABLE VI  
COMPOSITION OF CONCENTRATED STRIPPER CONDENSATE

Diol, wt. %	Lb. per 100 lb. of diol				Iron, molar
	Solids	Acid*	Ester*	NH <sub>3</sub>	
29.0	—	6.63	—	—	—
12.7	35.6	5.21	2.61	—	—
44.2	9.85	4.73	0.0	1.71	0.06
27.6	—	6.02	6.95	1.65	0.04

\*Calculated as acetic acid.

Crude diol was vacuum distilled in a small copper unit that consisted of a 25 gal. steam jacketed still pot and a 10 ft. column 6 in. in diam. packed with  $\frac{1}{2}$  in. raschig rings. Vapor from the still pot was admitted to the middle of the column. At the top of the column a coil provided reflux and at the bottom a steam jacket served as a reboiler. The unit was always operated batchwise and, to obtain better control, diol was removed from the top of the column rather than from the bottom. The steam to the reboiler was turned on full and two fractions, water and diol, were distilled, condensed, and collected in copper receivers.

*Crude Diol from Rectifying Column*

In purifying crude diol obtained from the base of the rectifying column, one distillation over sodium hydroxide, sufficient to neutralize the free and combined acid and to liberate the ammonia, reduced the total acid and ammonia to a negligible amount (0.02%). The evolved ammonia attacked the copper unit, and the water fraction was the deep blue color of the copper ammonium

complex. Calcium hydroxide was not satisfactory as a neutralizing agent because an excessive amount of sludge was formed and a large portion of the diol remained in the residue in the still pot. When sodium hydroxide was used, the contents of the still pot could be evaporated to almost complete dryness. The diol obtained by distilling the crude material over sodium hydroxide was a light brown color and two or three redistillations were required to produce a water white product. One distillation over sulphuric acid gave a clear product but dehydration products such as methyl ethyl ketone were formed (14). Even when colorless diol was prepared either by distillation over sulphuric acid or by repeated distillation over sodium hydroxide a color developed on standing.

#### *Crude Diol from Stripper Condensate*

The crude diol from stripper condensate was first distilled to separate the diol from the solids. Sodium hydroxide was not added to the crude because it caused excessive foaming during the distillation. The partially concentrated diol was then analyzed and sufficient sodium hydroxide was added to neutralize acids, saponify esters, liberate ammonia, and precipitate iron and copper. In the first distillation a sharp fractionation of acid occurred, giving a water fraction that was generally basic to phenolphthalein and a diol fraction with an acidity greater than that of the crude diol. Little or no decrease in total acid resulted. Both fractions contained some of the original ammonia but there was a loss of ammonia through the vacuum system during the distillation. Only traces of iron were found in the distillates, showing that iron was left with the residue of solids in the kettle. The water fraction, being slightly basic and ammoniacal, was always blue in color. The diol fraction, although usually containing considerable ammonia, was more acid than the other fraction and so had a lower copper content and a less intense blue color.

In the second distillation, carried out over sodium hydroxide, most of the acid, ester, and ammonia was removed. The water fraction was about 1% diol and the diol fraction was about 5% water. The water fraction was practically neutral and contained little or no ester. The diol was found to be uniformly low in acid and ester, about 0.01 N in acid and 0.02 N in ester. Ammonia was removed quite effectively and the amount left was almost entirely in the water fraction, leaving about 0.01 N ammonia in the diol as a maximum. This diol was either pale green to blue or colorless, and cations were present only in traces. Analytical data for one purification are presented in Table VII. The acid in the crude diol was 6.05% by weight of the diol present, expressed as acetic acid, and the acid content of the final product was 0.04%. Ester in the crude diol was 6.98% and was reduced to 0.09%. Ammonia was reduced from 1.65% to 0.01%.

Two samples of stripper condensate were purified by ion exchange resins in laboratory columns. Stripper condensate was used for the tests, as a dilute solution of diol must be used to maintain a low ester concentration. In commercial production where a scrubbing column would be used, the

TABLE VII  
PURIFICATION OF CRUDE DIOL BY DISTILLATIONS OVER SODIUM HYDROXIDE

Material	Gal.	Diol, wt. %	Acid, N	Ester, N	NH <sub>3</sub> , N	T.N.E.*	Color
Crude diol	11.0	27.6	0.277	0.320	0.268	0.953	
First distillation							
Water	4.7	0.04	Basic		0.023	0.023	Blue
Diol	6.0	52.9	0.456	0.00	0.434	0.890	Green blue
Second distillation**							
Water	4.25		Basic		0.087	0.087	Grey
Diol	1.80		0.011	0.011	0.010	0.032	Pale green

\*T.N.E. = Total neutralization equivalent = Sum of acid, ester, ammonia, and ferrous iron normalities.

\*\* Sufficient sodium hydroxide to neutralize the acid, ester, ammonia, and iron and a 10% excess was added.

product from the bottom of the scrubbing column would be passed through the exchanger beds. In the laboratory the condensate was passed through two cation exchangers in series and then through an anion exchanger column. The effluent was concentrated in a copper still to obtain a crude diol. This was further concentrated in glass apparatus and the diol was then distilled.

TABLE VIII  
PURIFICATION OF STRIPPER CONDENSATE BY ION EXCHANGE RESINS

Condensate:			
Diol, wt. %		1.64	1.88
Acid, normality		0.0156	0.0286
Ester, normality		0.00025	0.000
Acid, lb. m. eq. per 100 lb.		1.56	2.86
Ester, lb. m. eq. per 100 lb.		0.025	0.0
Acid, lb. m. eq. per 100 lb. diol		95.2	152
Ester, lb. m. eq. per 100 lb. diol		1.52	0.0
Crude diol:			
Diol, wt. %		27.8	16.0
Acid, lb. m. eq. per 100 lb. diol		3.54	2.84
Ester, lb. m. eq. per 100 lb. diol		0.98	1.84
Acid, lb. HOAc per 100 lb. diol		0.21	0.17
Ester, lb. HOAc per 100 lb. diol		0.059	0.11
Cations exchanged,			
lb. m. eq. per 100 lb. diol		63.1	68.2
Anions exchanged,			
lb. m. eq. per 100 lb. diol		159	220

The data for these experiments are given in Table VIII. The sum of the cations and anions exchanged is greater than the sum of the initial acid and ester because of the presence of inorganic salts in the condensate. A small amount of ferrous iron was present but the excess cations removed were largely ammonium ions. The diol obtained from the condensate of one test was distilled at atmospheric pressure. The high temperature resulted in the decomposition of organic material which was not removed by the exchangers, and the diol was a pale yellow in color. The diol from the second test was distilled at reduced pressure and a water white product, which has remained colorless on standing, was obtained. Although the acid and ester content of the diol obtained in these experiments was higher than that of diol purified by distillation over sodium hydroxide, the ion exchangers appear to have removed the impurities that cause color and unpleasant odor. If desired, the acid and ester content could be further reduced by conducting the final distillation over sodium hydroxide. From the required exchange capacities given in Table VIII the cost of an ion exchange process for diol purification was estimated to be 1.6 cents per pound. However, the additional cost over direct neutralization during distillation is about 0.4 cents per pound.

A water white product can be obtained by treatment with ion exchange compounds and distillation at reduced pressure in corrosion resistant equipment. Distillation over sodium hydroxide in copper equipment gives a product that has a pale yellow green color and is very low in acid, ester, ammonia, and metallic compounds.

Heat transfer coefficients from steam to boiling diol-water solutions were determined in the copper reboiler of the rectifying column at four concentrations, each at four different steam pressures. Plots of heat flux against diol concentration and temperature difference were constructed, and, by transferring from one plot to another, a plot was obtained of the over-all coefficient of heat transfer against temperature difference at various diol concentrations. Representative results are given in Table IX. The tubes of the calandria had been used for 18 months at the time of the tests and hence these values should be applicable to commercial operation.

TABLE IX

OVER-ALL COEFFICIENT OF HEAT TRANSFER FROM STEAM TO BOILING DIOL-WATER SOLUTIONS  
IN A CALANDRIA TYPE HEATING UNIT

Temperature difference, °F.	Weight per cent diol				
	0	20	40	60	80
	B.t.u. per hr. per sq. ft. per °F.				
30	306	273	225	—	—
50	360	305	255	205	175
70	375	300	250	215	175

## DRYING

A portion of washed and pressed bran was air dried to obtain samples for analysis. Stripping column residue was dried on an atmospheric double drum drier with drums 6 in. in diam. and 10 in. long. Samples of the dried residue were then analyzed. The performance of the drum drier is given in Table X and the results of the analyses are given in Table XI, together with analyses of commercial residues.

TABLE X  
PERFORMANCE OF LABORATORY ATMOSPHERIC DOUBLE DRUM DRIER

	Sample 1	Sample 2
Solids in feed, %	17.2	13.3
Feed rate, lb. per hr.	11.9	8.1
Drum speed, r.p.m.	3	2
Steam pressure, p.s.i. gauge	45	20
Feed rate, lb. per hr. per sq. ft. of drum surface	0.048	0.049
Lb. water evaporated per hr. per sq. ft. of drum surface	0.040	0.0425
Over-all heat transfer coefficient, B.t.u. per hr. per sq. ft. per °F.	0.6	1.1

TABLE XI  
ANALYSES OF PILOT PLANT AND COMMERCIAL RESIDUES\*

	Dried stripper residue		Dried screen solids	Distillers grains from rye	Brewers grains over 25% protein	Strained distillery slop**
	No. 1	No. 2				
Butanediol, %	1.27	1.58	0.53			
Moisture, %	8.42	11.8	10.7	7.2	7.5	10.0
Soluble solids, %	59.4	55.6	0.0			
Ash, %	11.7	13.5	1.65	3.9	3.5	6.6
Total nitrogen, %	5.59	6.02	1.21	3.7	4.24	4.91
Water soluble nitrogen, %	4.05	4.40	0.21			
Total P <sub>2</sub> O <sub>5</sub> , %	2.33	2.96	1.33	0.83	0.99	
Available P <sub>2</sub> O <sub>5</sub> , %	2.21	2.82	1.13			
Total K <sub>2</sub> O, %	0.11	0.10	0.07	0.24	0.09	
Total CaO, %	5.4	5.5	0.74		0.16	
Crude protein, % N × 6.25	34.9	37.6	7.56	23.1	26.5	30.7
Fat, %	5.1	5.0	3.4	7.8	6.9	15.4
Fiber, %	2.0	2.3	27.0	10.9	14.6	4.4
Nitrogen free extract, %	37.9	29.8	49.5	47.1	41.0	32.9
Thiamine, p.p.m.	0.0		0.0			
Riboflavin, p.p.m.	1.64		1.3			
Nicotinic acid, p.p.m.	88		6.4			

\* Thanks are due the Analytical Laboratory of the Division of Chemistry, National Research Council, to Dr. C. V. Marshall of the Department of Agriculture, and to Dr. Dyson Rose of the Division of Applied Biology, National Research Council, for analyses of the pilot plant residues. The analyses of the commercial residues were taken from Henry, W. A. and Morrison, F. B., *Feeds and Feeding*, 19th Edition, The Henry-Morrison Company, Ithaca, New York, 1928.

\*\* Calculated to a 10% moisture basis.

The ash content of the stripper residue was high because it contained all the calcium carbonate added to the mash. The butanediol values shown represent most of the diol originally present in the wet residues since only a small amount was removed in the drying process. The diol content of the residues may be reduced by more efficient stripping of the stripper residue or by more complete washing of the bran prior to drying. Oral toxicity tests of 2,3-butanediol were performed by Dr. L. I. Pugsley of the Department of National Health and Welfare on adult male rats. The tests showed that the lethal dose for 50% mortality was 11.5 ml. per kilogram of body weight. No tests were made to determine whether the effects are cumulative.

No thiamine was present in any of the solids. The riboflavin content of the stripper residue represents approximately 100% and the nicotinic acid content about 50% of the totals originally present in the wheat, although the residue was only 30% of the weight of the wheat. The bran contained about 50% of the amount of riboflavin and 100% of the nicotinic acid usually present in wheat brans. Comparisons of the nitrogen, phosphorus, and potash contents of the dried stripper residue with commercial fertilizers indicate that this material is of little value for this purpose. Although of a higher quality than dried manures, it could not compete with ordinary fertilizers without being enriched with either phosphorus or potash. The dried bran is of even less value as a fertilizer.

The dried stripper residue appeared to have considerable possibilities as a livestock feed. It was higher in protein and minerals than any of the commercial residues but somewhat lower in fat and fiber content. The composition of strained distillery slops corresponded most closely to that of the stripper residue. The dried bran is of little value as a food except as roughage.

#### Quantitative Flow sheet

For the purposes of cost estimates a quantitative flow sheet with estimates of the size of equipment was necessary. The flow sheet and cost estimates were based on a plant with a capacity of 1000 bu. per day. The flow sheet, with weights and compositions, is shown in Fig. 4, and the cost estimates are given in the following section. The composition of the fermented mash calculated for a 15% mash, 90% fermentation efficiency of wheat containing 50% starch, and a diol to ethanol ratio of 1.50 has already been given.

#### Ethanol Recovery

The diol and ethanol recoveries shown on the flow sheet are the same as those obtained in the pilot plant since the same column height, feed rate, and reflux ratio could be used. The steam to the preheater is that required to heat the mash to the boiling point. The details of concentrating and purifying the high wine are not shown but the cost of this operation was included in the cost estimates. The column, preheater, and condenser could be constructed of copper, as is customary in the distillery industry.

### *Screening and Pressing*

The material balance for the initial screening was calculated from the following values: total solids in slops, 6.61%; total solids in screenings, 13.5%; and ratio of insoluble solids to total solids in slops, 0.13. The screenings would then contain 9.73% of the diol and soluble solids and 21.5% of the total solids. If these screenings were pressed without washing, the diol loss would be 2.4% and diol content of the screenings on a dry basis would be 5.6%. Thus, washing would be required both to reduce the diol loss and to reduce the diol content of the dried bran.

If pressing is omitted, it is economical to supply wash water until the marginal diol recovery is such that the cost of evaporating the additional water equals the value of the diol recovered. Since washing does not change the ratio of diol to solids in the screen filtrate, adding wash water will affect only the evaporation. If the increase in fixed charges caused by the wash water is neglected, washing should be continued until the marginal weight of water required to recover one pound of diol is that given by the expression:

$$\frac{1000ae}{s},$$

where  $a$  is the value of diol in cents per pound,  $e$  is pounds of water evaporated per pound of steam, and  $s$  is the cost of steam in cents per 1000 lb. If  $a$  is 20,  $e$ , 1.70, and  $s$ , 25, washing should be continued until 1360 lb. of water is required to recover 1 lb. of diol. Adding water, however, decreases the diol recovered by pressing and it was found by trial calculations that a marginal diol recovery of 1 lb. per 750 lb. of water is a more economical recovery than 1 lb. per 1360 lb.

Fig. 4 shows a material balance for a washing with one equilibrium contact with an amount of water such that the marginal diol recovery is 1 lb. per 750 lb. of water. It was assumed that the total weight of screenings and the per cent insoluble solids would not change during washing. The material balance for pressing was calculated by taking the total solids concentration of the pressed bran to be 30.9%. The diol loss is 0.5% and the diol content of the bran on a dry basis is 1.33%.

### *Evaporation*

It is believed that any feed arrangement in a multiple effect evaporator would be technically satisfactory, and cost alone would determine the choice of an arrangement. Blom *et al.* (4) suggested a quadruple effect evaporator with a feed order of 2, 3, 4, 1 and Othmer *et al.* (16) suggested an order of 3, 2, 1 for a triple effect evaporator. Each effect would be surmounted by a rectifying column to prevent diol from being lost in the vapor. The vapor-liquid equilibria data of the system *levo*-2,3-butanediol-water were reported by Knowlton (9) for pressures below and just slightly above atmospheric. Measurements at pressures ranging from 14.7 to 75 p.s.i. abs. were reported by Tomkins *et al.* (20).

Calculations for this operation for the quantitative flow sheet were based on a double effect evaporator with forward feed. Rough estimates were made of total materials and diol concentrations using over-all coefficients of heat transfer of 800 and 300 B.t.u. per hr. per sq. ft. per °F. It is expected that higher values than those obtained in the pilot plant kettle would be obtained with vertical tube evaporators. (The evaporation of screened distillery slops has been described by Herman *et al.* (8).) Approximate economical reflux ratios were calculated for the two rectifying columns, and the complete material distribution was then calculated by means of heat and material balances. From the initial and operating costs of this double effect evaporator it was estimated that the economical number of effects is 2.4.

Since both the distillate and syrup are acidic, an acid resistant material should be used in fabricating the evaporator bodies, columns, and piping. If lime or other alkali is not added to the filtrate, copper or copper base alloys would be satisfactory. If alkali is added, the syrup and distillate will contain free ammonia and most copper base alloys would be unsatisfactory. Stainless steel and monel would give least corrosion, but iron and steel might prove to be satisfactory if sufficient alkali were used. Standard iron pipe was satisfactory for handling cold filtrate in the pilot plant.

Whether or not the diol in the vapor from the final feed effect of a large scale evaporator would be recovered by rectification or returned to the syrup depends on economic factors. Forward, backward, or mixed feed could be used and the final column could be operated at one of a number of different pressures. The diol recovered could be mixed with the diol from a stripping-scrubbing operation, ethanol precipitation, or any other recovery step used to recover diol from syrup. Material distributions could be calculated by material balances with the aid of vapor-liquid equilibria data.

#### *Stripping and Scrubbing*

In commercial production, over-all continuous operation of a stripping column would be obtained by means of a storage tank between the evaporator and the stripping column, to allow the syrup to accumulate while the column was being cleaned. This would be cheaper than installing two stripping columns and operating one while the other was being cleaned but the operation would be more difficult. Since the cost of cleaning a stripping column would be very small the flooding time is not important in choosing commercial operating conditions. The most important factor is the size of the column, which is determined by the solids content of the syrup and the syrup and steam rates. For a plant of a given size the average solids throughput per day or hour is a constant; thus the column diameter will be smaller at higher solids concentrations for the same syrup mass velocity. The number of transfer units, column height, and column diameter were calculated for a feed rate of 160 lb. per hr. per sq. ft. and a steam rate of 610 lb. per hr. per sq. ft. at the three solids concentrations for which flooding times are given in Table III. The diol concentration of the syrup was calculated from the solids concentration and the ratio of diol to solids. The diol lost in the

residue was set at 80 lb. per day, and the diol concentration of the vapor at the top of the column was calculated from a material balance. The number of transfer units was then computed as described previously. The height of a transfer unit was taken as 4 ft. for all concentrations. When diol concentrations were calculated for a feed rate of 210 lb. per hr. per sq. ft. and a steam rate of 610 lb. per hr. per sq. ft., it was found that these conditions were inoperable for the recovery desired. Operation at a solids content of 23.6% required both a shorter and a smaller column than the lower concentrations. Since the packing is the main item in the cost of a packed column and since the cost of auxiliary equipment would be almost the same for all concentrations, this concentration would give the lowest initial cost. Neglecting the cost of cleaning, which would be small, the operating costs for the three solids concentrations would be almost equal. Thus, the highest of the three solids concentrations would give the lowest total cost.

A solids concentration of 23.6% and the above feed rates and assumptions were therefore used for the quantitative flow sheet and cost calculations. The equilibrium and the stripping and scrubbing column operating lines used for these calculations are shown in Fig. 3. The estimated dimensions of the two columns are: 5.75 ft. in diam. by 37 ft. high for the stripping column,

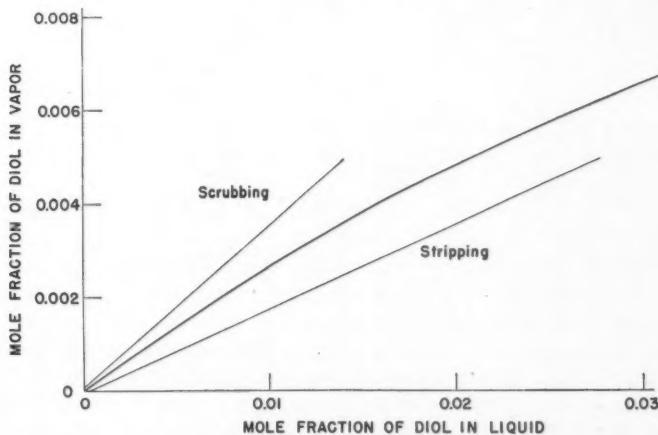


FIG. 3. Design diagram for stripping and scrubbing operations.

and the same diam. by 55 ft. high for the scrubbing column. The shells of the columns could be constructed of Ni-resist cast iron or steel but a stainless steel or monel clad steel would be better. If a bubble cap scrubbing column were used it should be constructed of an acid and ammonia resistant alloy such as stainless steel or monel.

From Fig. 4 it can be seen that the steam fed to the bottom of the stripping column is recovered at the top of the scrubbing column. The pressure of the recovered steam will be only slightly lower than the pressure of the inlet steam.

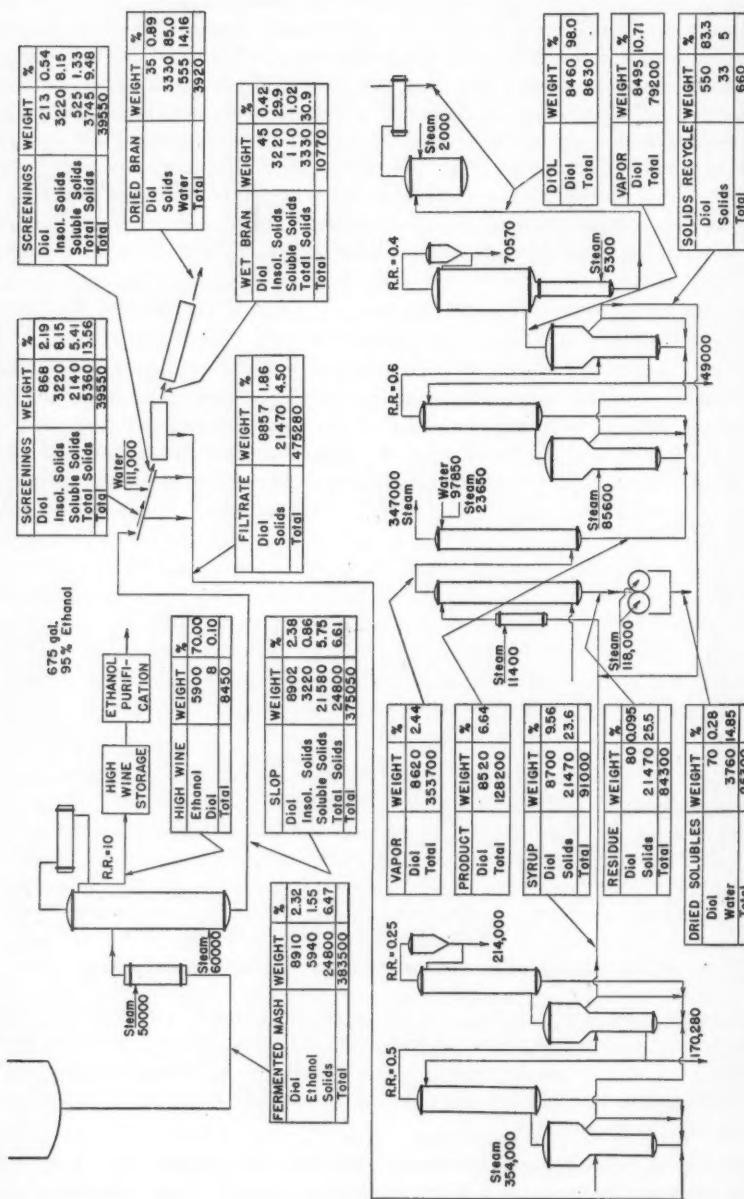


FIG. 4. Quantitative flow sheet for commercial production of levo-2,3-butadieniol (basis: 1000 bu. of wheat per day).

The recovered steam could be used for the evaporators, or as shown by Callahan (5) a thermo-compressor could be used and the steam recycled. In both, the actual steam consumption of the stripping-scrubbing step is low.

#### *Concentration and Purification*

The most economical method to be used in commercial production for concentrating the scrubbing column product to 97-99% diol depends on the size of the plant. One method would be to feed the liquid scrubbing column product to a rectifying column operated at atmospheric pressure. The bottom product, containing 60 to 80% diol would then be vaporized, the vapor rectified at reduced pressure to 97-99% diol, and the liquid product would then be redistilled at reduced pressure. A second method would be to concentrate the scrubbing column product to 60-80% diol in a double effect evaporator with rectifying columns mounted on each effect. This partially concentrated product would then be vaporized, rectified, and redistilled. A third method would be to feed the vapors from the final effect of a multiple effect evaporator to a distillation column as is shown in Fig. 4. The first of these methods would have the lowest initial cost but the highest operating cost, while the second would have the highest initial cost and lowest operating cost. Thus, the first would be favored for a small plant and the second for a large plant. Approximate calculations showed that for a plant with a capacity of 1000 bu. per day the total costs of the three methods are almost equal. The third one, which is intermediate in both initial and operating costs, was chosen for illustrative purposes.

Initial approximations and methods of calculation similar to those used in computing the material distribution for the screen filtrate evaporator were used for this operation. Over-all coefficients of heat transfer of 800 and 400 B.t.u. per hr. per sq. ft. per °F. were assumed for the two effects. Since the scrubbing column product would contain a small amount of solids, they must be withdrawn from the second effect and recycled with the syrup. An estimate of the amount and composition of the recycled material is shown in Fig. 4 but it is not included in the stripping, scrubbing, and concentrating operations. If ion exchangers were used for purification they would be placed between the scrubbing column and the evaporator. If direct neutralization were used, sodium hydroxide would be added to the second effect of the evaporator. In either method a small amount of sodium hydroxide would be added to the final distillation evaporator.

Copper or copper base alloys could be used for the concentration equipment up to the point where sodium hydroxide is added. For the final stage of the concentration and the redistillation of the product the material of construction should be resistant to acids and ammonia. Lead and zinc are not satisfactory.

#### **Cost Estimates**

The pilot plant work has shown that recovery of *levo* 2,3-butanediol from whole wheat mashes fermented by *A. polymyxa* is technically feasible. The quantitative flow sheet shown in Fig. 4 was prepared for the purpose of cost

estimates and to illustrate the distribution of materials described in the experimental section. The data and assumptions used in computing the flow sheet have already been stated. In preparing cost estimates it was necessary, of course, to include mashing and fermenting operations. A plant with a capacity of 1000 bu. a day would require five cookers with a capacity of 1500 gal. each, four or five 500 gal. propagators and 10 fermenters with a fermenting capacity of 20,000 gal. each. The initial cost was estimated to be \$500,000.00 (1945), which is \$500.00 per daily bushel of wheat or \$304.00 per yearly ton of diol. Raw material, steam, water, power, labor, and products produced are given in Table XII. In addition to labor, the plant would require a management staff of administrative and technical personnel and assistants. A management cost of \$105.00 per day was allowed in the estimate.

TABLE XII  
RAW MATERIALS, ENERGY REQUIREMENTS, AND PRODUCTS  
(Basis: 1000 bu. of wheat per day)

Raw materials	
Wheat	1000 bu.
Calcium carbonate	2500 lb.
Malt	300 lb.
Sodium hydroxide	1000 lb.
Turkey Red Oil	50 lb.
Energy and power	
Steam	750,000 lb.
Water	.850,000 gal.
Electric power	3500 kwh.
Labor	300 man-hours
Products	
<i>levo</i> -2,3-butanediol	8460 lb.
Ethanol, 95%	675 gal.
Dried grains (14.16% water)	3920 lb.
Dried solubles (14.85% water)	25300 lb.

The selling price of butanediol in dollars per gallon is given by the expression.

$$S.P. = \frac{1}{846} (1000A + 7.5B + 35C + 300D - 1.96E - 12.65F - 6.75G + 16.67H + 684)$$

where  $A$  = Cost of wheat, dollars per bushel;

$B$  = Cost of steam, cents per 1000 lb.;

$C$  = Cost of power, cents per kwh.;

$D$  = Cost of labor, dollars per man-hour;

$E$  = Selling price of dried grains, dollars per ton;

$F$  = Selling price of dried solubles, dollars per ton;

$G$  = Selling price of 95% ethanol, cents per gal.;

$H$  = Profit, % of initial cost (\$500,000).

The constant, 684, includes factors not given by the variables in the expression, and 846 is the final diol yield in imperial gallons per 1000 bu. A depreciation rate of 2% was assumed for the building (\$100,000) and 7% for the plant equipment.

With wheat at \$1.10 per bu., steam at 25¢ per 1000 lb., electric power at 1¢ per kwh., labor at \$1 per man-hour, dried bran and solubles at \$30 per ton, and 95% ethanol at 60¢ per gal. the cost of production of butanediol is \$1.73 per gal. or 17.30¢ per lb. The distribution of costs and credits at the conditions listed above is shown in Table XIII. With wheat at \$1.00, \$1.25, and \$1.50 per bu. and all other costs and prices as above, the cost of production of butanediol is 16.1, 19.1, and 22.1¢ per lb., respectively.

TABLE XIII  
COST AND CREDIT DISTRIBUTION FOR PRODUCTION OF BUTANEDIOL

Distribution	Percent of total	Cents per imp. gal.
Costs		
Fixed costs	14.30	39.10
Wheat	47.70	130.10
Other raw materials	5.46	14.89
Steam	8.15	22.20
Wages	13.00	35.50
Other production costs	11.39	31.13
	100.00	272.83
Credits		
Butanediol	63.8	173.15
Ethanol	17.2	47.88
Dried solids	19.0	51.80
	100.0	272.83

C. T. Langford (10) has given the cost of *levo*-2,3-butanediol as 10.62¢ per lb. This is based on a plant with a capacity of 8,500 bu. per day, a diol yield of 9.86 lb. per bu., and a grain cost of 70¢ per bu. The initial cost of the plant is \$240 per yearly ton of diol. The higher yield is probably due to the assumption of a higher starch content of the grain. If a yield of 8.46 lb. per bu. and a grain cost of \$1.10 per bu. had been used in Langford's estimate, the cost of butanediol would have been 16.5¢ per lb. (The cost of production of the *meso*-isomer would be appreciably less than that of the *levo*- because a larger portion of the starch is converted to diol and a smaller portion to ethanol.)

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many of the sub-contracts. Mr. J. Cody and Mr. R. E. MacMorran and their staffs, of the Division of Mechanical Engineering, National Research Laboratories, erected and serviced the pilot plant. Dr. Dyson Rose and Mr. W. S. King of this Division assisted in directing the installation of the units and also in initial operations. Finally, thanks are due the operational and laboratory staff of the pilot plant.

### References

1. ADAMS, G. A. and LESLIE, J. D. Can. J. Research, F, 24 : 12-28. 1946.
2. BLACKWOOD, A. C., WHEAT, J. A., LESLIE, J. D., LEDINGHAM, G. A., and SIMPSON, F. J. In preparation.
3. BLOM, R. H., MUSTAKAS, G. C., EFRON, A., and REED, D. L. Ind. Eng. Chem. 37 : 870-872. 1945.
4. BLOM, R. H., REED, D. L., EFRON, A., and MUSTAKAS, G. C. Ind. Eng. Chem. 37 : 865-870. 1945.
5. CALLAHAM, J. R. Chem. & Met. Eng. 51, No. XI: 94-98. 1944.
6. COLBURN, A. P. Trans. Am. Inst. Chem. Engrs. 35 : 211-236. 1939.
7. CORNWELL, R. T. K. U.S. Patent No. 2,390,779. Dec. 11, 1945. Chem. Abstracts, 40 : 1277. 1946.
8. HERMAN, A., STALLINGS, E. M., and WILKIE, H. F. Trans. Am. Inst. Chem. Engrs. 38 : 791-812. 1942.
9. KNOWLTON, J. W., SCHIELTZ, N. C., and MACMILLAN, D. J. Am. Chem. Soc. 68 : 208-210. 1946.
10. LANGFORD, C. T. Eleventh Annual Chemurgic Conference. March 18, 1946. St. Louis, Mo. Chemurgic Papers, Series No. 3, No. 465. 1946.
11. LESLIE, J. D. and CASTAGNE, A. Can. J. Research, F, 24 : 311-319. 1946.
12. LIEBMANN, A. J. Oil & Soap, 22 : 31-34. 1945.
13. LIEBMANN, A. J. and DE BECZE, G. U.S. Patent No. 2,389,263. Nov. 20, 1945. Chem. Abstracts, 40 : 9798. 1946.
14. NEISH, A. C., HASKELL, V. C., and MACDONALD, F. J. Can. J. Research, F, 23 : 281-289. 1945.
15. OTHMER, D. F., BERGEN, W. S., SHLECHTER, N., and BRUINS, P. F. Ind. Eng. Chem. 37 : 890-894. 1945.
16. OTHMER, D. F., SHLECHTER, N., and KOSZALKA, W., Ind. Eng. Chem. : 37 : 895-900. 1945.
17. REICH, G. T. Chem. & Met. Eng. 44 : 131-133. 1937.
18. SENKUS, M. Ind. Eng. Chem. 38 : 913-916. 1946.
19. TOLLEFSON, E. L., WHEAT, J. A., and LESLIE, J. D. Can. J. Research, F, 24 : 300-310. 1946.
20. TOMKINS, R. V., WHEAT, J. A., and STRANKS, D. W. Can. J. Research, F, 26 : 168-174. 1948.
21. WALMESLEY, R. A. and DAVIS, W. R. U.S. Patent No. 2,397,065. March 18, 1946. Chem. Abstracts, 40 : 3224. 1946.
22. WARD, G. E., PETTJOHN, O. G., LOCKWOOD, L. B., and COGHILL, R. D. J. Am. Chem. Soc. 66 : 541-542. 1944.

## PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

### XXIX. PILOT PLANT STUDIES ON FERMENTATION OF BARLEY BY *AEROBACILLUS POLYMYXA* AND RECOVERY OF THE PRODUCTS<sup>1</sup>

BY R. V. TOMKINS,<sup>2</sup> D. S. SCOTT,<sup>2</sup> AND F. J. SIMPSON<sup>3</sup>

#### Abstract

Barley mashes were successfully fermented by *Aerobacillus polymyxa* on a pilot plant scale. In the laboratory a 12.5% mash appeared to be optimum but more concentrated mashes were efficiently fermented in the pilot plant. The hulls caused some mechanical difficulties, but these were overcome by eliminating right angle joints in the piping and by screening before recovery operations. Products were recovered by the same operations as for wheat. The lower raw material cost of barley resulted in an estimated reduction in the production cost of *levo*-2,3-butanediol of 7%, based on 1947 prices; or a reduction of 10%, based on a long-term average for 1908-1940.

#### Introduction

The fermentation of wheat by *Aerobacillus polymyxa* has been thoroughly investigated both in the laboratory and the pilot plant to determine the feasibility of producing *levo*-2,3-butanediol on a commercial scale. A cost estimate based on this work for a plant to process 1000 bu. per day of wheat (5) showed almost half the cost of production to be due to the cost of the basic raw material. It was therefore considered desirable to assess the possibility of using western feed barley, which is a good source of starch and somewhat cheaper than feed wheat, as the substrate for the fermentation.

Some average analyses of wheat and barley are compared in Table I. These data are from Henry and Morrison (4) with the exception of the starch values, which are from analyses made in the National Research Laboratories.

TABLE I  
PER CENT COMPOSITION OF WHEAT AND BARLEY  
(All values on a moisture-free basis)

Component	Wheat	Barley
Ash	2.1	3.0
Crude protein	13.8	12.7
Fiber	2.4	5.1
Fat	2.3	2.3
Starch	58.0	51.8

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<sup>2</sup> Chemical Engineer, Industrial Utilization Investigations.

<sup>3</sup> Bacteriologist, Industrial Utilization Investigations.

### Fermentation

Barley mashes of various concentrations were fermented in the laboratory before large scale tests were begun. The desired amounts of ground grain and water were slurried together with 1% calcium carbonate, and 300-ml. amounts were placed in 500 ml. Erlenmeyer flasks and sterilized for one hour at 120° C. These samples were inoculated with 5 ml. of a 24 hr. culture of a barley medium, using the strain (C42-3) of *Aerobacillus polymyxa* that had given consistently good results with wheat. The mashes were incubated for 72 hr. at 32° C. and then examined and analyzed for products.

A mash concentration of 12.5% barley gave the most efficient fermentation (Table II). Mashes of higher concentration were very thick and 'jelled' into a solid mass. Such mashes remained in the jelled state for 24 to 48 hr.

TABLE II  
EFFECT OF BARLEY MASH CONCENTRATION ON YIELD AND FERMENTATION EFFICIENCY  
(300-ml. fermentations at 32° C.)

Mash concentration, %	Yield, lb./bu. (48 lb.)		Diol-alcohol ratio	Efficiency, %
	Diol	Alcohol		
10	5.5	4.3	1.3	78
12.5	6.4	5.7	1.1	96
15	6.1	4.5	1.4	84
17.5	5.4	3.6	1.5	72
20	5.1	2.9	1.8	64

after inoculation, then they broke up and fermented at a rapid rate, as shown by the production of gas. When the mash concentration had been properly adjusted, no further difficulty was experienced in fermenting barley mashes in the laboratory.

The fermentation procedure followed in the pilot plant was the same as that developed for wheat (2). The grain was ground in an attrition-type mill, metered into a mixing barrel with the required amount of water, and the slurry pumped to the cooker. The mash was sterilized for two hours at 120° C., then blown to a sterile fermenter. After cooling, 25 lb. of separately sterilized calcium carbonate was added, and the mash inoculated with two liters of a 24 hr. culture similar to that described for the wheat fermentation (1), with barley replacing the wheat. The final volume of the mash averaged 450 gal. The fermenter was maintained at 32° C., with agitation during the first 24 hr. At 96 hr. the fermentation was considered complete.

During the fermentation, samples were taken at 24-hr. intervals. The course of the barley fermentation was found to be similar to that of the wheat, average values being: 70% complete at 48 hr., 80% at 72 hr., and 90% at 96 hr. The pH trend was also similar, dropping sharply from an initial pH of 6.5, to 5.5-5.7 in 24 hr. with a final pH at 96 hr. of 5.3-5.7.

A summary of the final yields and efficiencies is given in Table III. The diol-alcohol ratio and efficiencies (see (2) for method of calculation) for the

TABLE III  
FERMENTATION YIELDS AND EFFICIENCIES OF BARLEY MASHES AFTER 96 HR. INCUBATION  
AT 32° C.  
(440-gal. fermentations at 32° C.)

Mash conc., %	Yield, lb./bu. (48 lb.)		Diol-alcohol ratio	Efficiency*, %
	Diol	Alcohol		
7.5	5.6	5.1	1.1	85
11.5	7.0	3.6	1.9	84
12.1	5.9	4.3	1.4	81
13.1	6.5	4.8	1.4	90
14.0	6.9	5.0	1.4	94
14.2	6.6	4.3	1.4	87
14.5	5.9	4.1	1.4	80

\* Based on 47.3% starch in the barley.

barley are of the same order as those for wheat mashes of the same concentration. As the efficiencies are based only on total products and starch content of the mash, they are directly comparable to similar figures for wheat fermentations (2). Efficient fermentations were obtained with higher mash concentrations in the pilot plant than in the laboratory.

Some difficulty was encountered in the pilot plant when attempts were made to slurry the ground barley in the equipment used for wheat. A large portion of the barley hulls passed through the attrition-type grinder practically intact, and plugged the lines wherever sudden changes in direction or abrupt constrictions occurred. By altering the pipe, barley mashes up to 14.5% were slurried without difficulty. In commercial practice, the use of streamline pipe up to the point of removal of the hulls, or a grinder that would completely comminute the hulls, would probably solve this difficulty.

#### Recovery of Products

The same operations used in the recovery of alcohol and butanediol from wheat mashes were used for the barley mashes, with only a minor change in sequence. The fermented wheat mashes were stripped of alcohol in a beer still, the slop screened, and the filtrate concentrated with rectification. When barley was used, it was necessary to screen the fermented mash as the first step in order to remove the hulls, i.e., the mash was taken directly to a vibrating screen from the fermenters, and the filtrate was then sent to the beer column for alcohol removal. The remaining steps of the recovery process were the same as those for wheat mashes (5).

The 100 mesh screen and press rolls used removed 15% of the total solids from a wheat mash, but 35% of the total solids from a barley mash. This resulted in a screen filtrate having a butanediol-solids ratio of about 0.5, as compared with 0.4 for wheat. The results of several screening runs are given in Table IV.

TABLE IV

EFFECT OF BARLEY MASH CONCENTRATION ON SOLIDS REMOVED BY SCREENING, AND DIOL-SOLIDS RATIO OF THE FILTRATE

Mash conc., %	Total solids, lb.	Screen and press solids, lb.	Filtrate solids, lb.	Solids removed, %	Filtrate, diol-solids ratio
7.5	83.8	32.2	51.6	36.6	0.511
12.1	193.3	60	133.3	31.0	0.565
13.1	215.0	73	142	34.0	0.502
14.2	251.1	92.6	158.5	37.0	0.564

The bran (or insoluble solids) fraction from the barley was, of course, larger than that from wheat. The syrup obtained on evaporation of the filtrate contained 30 to 40% more butanediol than a wheat syrup of the same solids content. This would result in a correspondingly smaller amount of syrup, with a consequent reduction in the size of the stripping and scrubbing equipment required. The higher butanediol concentration in the syrup would also allow a scrubber product of higher butanediol concentration, so that less water would have to be evaporated to produce the final product. Since the bran fraction is larger, the stripper residue obtained will be less from a barley syrup than that from a wheat syrup. Unfortunately, the savings mentioned above are small compared with other costs (*vide infra*).

The composition of the residues obtained in the wheat and barley fermentations are given in Table V. Protein and fiber contents are substantially the

TABLE V  
COMPOSITION OF CRUDE FERMENTATION RESIDUES, %

Residue	Wheat	Barley
Bran or hulls		
Protein	7.6	7.5
Ash	1.7	4.0
Fat	2.9	0.6
Fiber	29.0	25.1
Stripper residue		
Protein	36.2	38.6
Ash	12.6	17.7
Fat	3.6	6.5
Fiber	2.2	1.6

same for the comparable products of each fermentation. The barley products contain considerably more ash. The evaluation of wheat residues as fertilizers or feeds given by Wheat *et al.* (5) appears to apply equally well to the barley residues.

### Estimate of Costs

Various wheat and barley statistics based on the long-term average for the period 1908-1940 are given in Table VI. All data were taken from the Canada

TABLE VI  
WHEAT AND BARLEY STATISTICS  
(Based on average values, 1908-1940)

Cost and yield values	Wheat	Barley
Price, cents/bu.	87	51
Price, cents/lb.	1.47	1.06
Price, cents/lb. starch*	2.83	2.26
Yield, bu./acre	15.6	23.3
Yield, lb. starch/acre	487.0	526.0
Yield, dollars/acre	13.6	11.9

\*Basis: Wheat, 52%; barley, 47% starch as received.

Year Book (3). On this basis, barley gives a higher yield of starch per acre than wheat, but the monetary return to the grower is less. Cost estimates based on the fermentation of wheat (5) showed that the raw material cost is about one-half of the total cost of butanediol. Therefore, the percentage reduction in the cost of butanediol would be one-half the percentage reduction in the cost of starch.

A comparison of the product yields of wheat and barley fermentations are given in Table VII and the comparative cost estimates based on current and

TABLE VII  
COMPARISON OF YIELDS OF WHEAT AND BARLEY FERMENTATIONS  
(Basis: 30 tons per day—1000 bu. wheat or 1250 bu. barley at 13.5% moisture)

Products	Wheat	Barley
Butanediol recovered, gal.	846	781
Alcohol recovered, gal. 95%	675	610
Bran or hulls, 13.5% moisture, tons	1.89	5.12
Residue, 13.5% moisture, tons	12.20	9.53
Total residues	14.09	14.65

TABLE VIII

COMPARISON OF COSTS OF WHEAT AND BARLEY FERMENTATIONS  
(Basis: 30 tons per day—1000 bu. wheat or 1250 bu. barley at 13.5% moisture)

Production costs and credits	Wheat		Barley	
	Present	Long-term average	Present	Long-term average
Costs	\$	\$	\$	\$
Grain*	1270.00	870.00	1025.00	637.50
Utilities (steam, power, water)	265.00	265.00	261.00	261.00
Other costs (wages, fixed costs, etc.)	941.50	941.50	941.50	941.50
Total daily cost	2476.50	2076.50	2227.50	1840.50
Credits	\$	\$	\$	\$
Ethanol at \$0.60 per gal.	405.00	405.00	366.00	366.00
Residues at \$30.00 per ton	422.70	422.70	439.50	439.50
Butanediol	1648.80	1248.80	1422.00	1035.00
	¢	¢	¢	¢
Cost butanediol per lb.	19.5	14.8	18.2	13.3

\* Wheat—present price, \$1.27 per bu.; long-term average, \$0.87 per bu. Barley—present price, \$0.82 per bu.; long-term average, \$0.51 per bu.

long-term average prices are given in Table VIII. All costs and credits have been taken from the figures given by Wheat *et al.* (5). These estimates show that at present Western Canadian prices (1947) a saving of 7.0% would result from the substitution of barley for wheat in the *Aerobacillus polomyxa* fermentation, and on the basis of long-term average grain prices a 10% cost reduction could be expected. As was previously mentioned, the use of barley also makes other savings possible.

### References

1. BLACKWOOD, A. C. and LEDINGHAM, G. A. Can. J. Research, F, 25 : 180-191. 1947.
2. BLACKWOOD, A. C., WHEAT, J. A., LESLIE, J. D., LEDINGHAM, G. A., and SIMPSON, F. J. In preparation.
3. DOMINION BUREAU OF STATISTICS. The Canada year book 1943-44. Edmond Cloutier, Ottawa. 1944.
4. HENRY, W. A. and MORRISON, F. B. Feeds and feeding, 19th ed. The Henry Morrison Company, Ithaca, New York. 1928.
5. WHEAT, J. A., LESLIE, J. D., TOMKINS, R. V., MITTON, H. E., SCOTT, D. S., and LEDINGHAM, G. A. Can. J. Research, F, 26 : 469-496. 1948.





